

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in the Catalytic Cracking of Hydrocarbon Oils

WE, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the cracking of hydrocarbon oils to form lower boiling motor fuel products and pertains more particularly to the cracking of hydrocarbon oil in the presence of a finely divided catalyst suspended in the oil to be cracked.

It has heretofore been proposed to catalytically crack hydrocarbon oil by suspending the catalyst in finely divided form in the oil stream to be cracked and passing the resulting suspension through a cracking zone. In some cases the catalyst is mixed with the oil in liquid form to form an oil-catalyst slurry and the resulting slurry passed through a vaporizing and cracking zone. In other cases, the oil is first vaporized and the catalyst is injected into the stream of oil vapors passing to the cracking zone. In either case the finely divided catalyst must eventually be separated from the cracked product. It is desirable in most cases to separate as much of the powdered catalyst from the cracked product as possible while the latter is in vapor form. As a practical matter however, it is difficult, if not impossible, in large scale operation to recover 100% of the catalyst from the oil vapor without any condensation of the latter since some of the extremely fine material remains entrained within the vapor and cannot be readily removed. This material ultimately appears in the condensate formed by fractionating the cracked product.

It has heretofore been proposed to recover this material from the condensate by filtering the condensate and then distilling the filter cake to remove the oil and afterwards regenerating the catalyst. As a practical matter however, the cost of

recovery makes this procedure more or less uneconomical.

The present invention is applicable to processes in which finely divided catalytic material suspended in the vaporised oil is passed through a cracking zone maintained at cracking temperature and the suspension is maintained within said zone for a length of time sufficient to obtain the desired conversion.

The resulting suspension of cracked products and powdered catalyst is passed through one or more solid-gas separators such as cyclone separators for removal of powdered materials therefrom. These solid gas separators are maintained at a temperature which will avoid any substantial condensation of cracked vapors during their passage therethrough. During the passage of the suspension through the separator the bulk of the powdered catalyst is separated in relatively dry state from the hydrocarbon vapors. The cracked vapor after passing through the solid-gas separator wherein the bulk of the powdered material is removed therefrom is then passed into a cooling zone wherein the temperature of the product is reduced to a point where a small fraction of the heavy oil vapors is condensed. This cooling may be accomplished in a heat exchanger, fractionating, or baffle tower wherein condensates formed during the cooling serve as a washing medium for removing the final traces of catalyst from the stream of vaporised oil. When operating in this manner, the first condensate fraction, which may amount to from 1 to 20% of the total vapors will contain the catalyst entrained in the oil vapors leaving the separator. This fraction is segregated from the remainder of the cracked products.

According to the invention, the heavy condensate fraction so segregated and containing the entrained catalyst therein is subjected to further cracking in the same or a different cracking unit. For example, this fraction may be subjected to separate cracking under conditions such as to form a substantial amount of gasoline as a final product or under conditions controlled to produce a gas oil for further

catalytic cracking with a minimum conversion into gasoline. This condensate containing the residual catalyst may be cracked by itself or it may be mixed with 5 other feed. Moreover, additional catalytic material may be added to the oil. However, this fraction may be recycled to the same cracking zone or separately vaporized and then recycled to the same 10 cracking zone.

Having set forth the general nature and objects, the invention will be better understood by reference to the accompanying drawing which is partially 15 schematic and partially diagrammatic illustration of an apparatus suitable for carrying the invention into effect.

Referring to the drawing, the reference character 10 designates the charge line 20 through which the oil to be cracked may be introduced into the system. This oil may comprise for example a clean condensate stock such as virgin gas oil or a residual stock containing unvaporizable 25 constituents.

The oil introduced in the system through line 10 is forced by means of pump 11 to a heating coil 12 located in the furnace 13 in which it is heated to a 30 perature sufficient to vaporize a substantial amount of the oil. If desired, a vaporizing medium such as steam or other stripping gas may be introduced into the heating coil 12 to assist in vapor- 35 izing the oil.

The oil after passing through the heating coil 12 is transferred by means of a transfer line 14 leading to a separator 15 40 in which oil vapors are separated from unvaporized residue. In cases where the feed stock is a substantially completely vaporizable oil the separator 15 may be omitted or the product from the heating coil 12 by-passed around the separator 45 through line 16.

Residue separated in the separator 15 is withdrawn therefrom through line 17 and may be rejected from the system or treated as later described. Vapors liberated in 50 separator 15 pass overhead therefrom through line 18 and may be passed through a superheating coil 19 located in furnace 20 to further heat the oil to the desired reaction temperature. In cases 55 where a clean condensate stock is employed as a feed stock to the cracking unit, the oil may be heated in coil 12 to the desired reaction temperature. In such case, the superheater 19 may be omitted 60 or the oil by-passed around the superheater through line 21 and passed directly to a cracking converter 22.

The oil after being preheated to the desired cracking temperature is inter- 65 mixed with a finely divided cracking

catalyst in an amount sufficient to obtain the desired catalytic effect. The relative amount of catalyst introduced into the oil stream will depend upon a number of 70 factors such as the nature of the stock to be cracked, the activity of the catalyst, temperature of the cracking zone, the time of contact of the oil vapors within the reaction zone, etc. In general the amount of catalysts may vary between .5 75 parts of catalyst per part of oil to 10 parts of catalyst per part of oil.

The catalyst employed may be any desired cracking catalyst in finely divided form such as for example naturally active 80 or activated clays or synthetic compounds having similar chemical components. Any suitable means may be provided for injecting the powdered material into the oil stream. As illustrated, there is shown a 85 screw conveyor 23 for feeding the catalyst into the line leading into the converter. The catalyst from the hopper 24 may be fed into the screw conveyor at any desirable rate by a suitable feeding mechanism 90 such as a star feeder 25.

The oil vapors containing the finely divided catalyst in suspension therein are passed through the converter 22 at a 95 velocity sufficient to maintain the catalyst in suspension within the vapors. It is not essential to the present invention that the resident time of the catalyst and oil vapors within the converter 22 be the same. The density of the suspension may 100 be such that the catalyst travels at a slower rate through the reaction zone than does the oil vapors.

The converter may be of any suitable 105 design capable of maintaining the material in suspension such as a vertical tower as illustrated or an elongated coil either heated or unheated.

After passing through the converter 22 110 the cracked product containing the catalyst in suspension therein is transferred through line 26 to a suitable solid-gas separating equipment. Such separating equipment may comprise for example 115 three cyclone separators 27, 27' and 27'' arranged in series. The separators are maintained at a temperature which will avoid any substantial condensation of the cracked vapors during their passage 120 therethrough. Powdered catalyst separated in the separators is removed through conduits 28, 28' and 28'' having suitable 125 sealing mechanism capable of maintaining a pressure seal such as a star feeder 29, 29' and 29''. The catalyst so separated will normally be contaminated with carbonaceous deposits formed during the cracking operation. This catalyst is preferably regenerated by burning off the carbonaceous deposit in any suitable 130

equipment and the regenerated catalyst is then returned to the hopper 24 for further use.

The cracked vapors having the bulk of the powdered material removed therefrom in the separators 27, 27' and 27" but still containing substantial amounts of entrained particles is then passed through line 31 to the lower section of a fractionating tower 32 wherein the vapors are subjected to cooling and fractionation to condense insufficiently cracked constituents thereof.

The fractionating tower 32 may be of any suitable condensation capable of bringing about fractional condensation such as for example a bubble tower.

The initial condensate formed in the bottom section of the fractionating tower is segregated from the condensate formed in the upper portion of the tower. This condensate contains any residual catalyst which may be entrained in the oil vapor leaving the final separator 27'.

In order to segregate the heavy condensate fraction from the remainder of condensate formed in the tower the fractionating tower 32 is provided with a trap-out tray 33 which collects condensate formed in the upper section of the tower. The heaviest condensate containing the entrained catalyst is withdrawn from the bottom of the tower through line 34 and is treated as hereinafter described.

Condensate formed in the upper section of the tower 32 above the trap-out tray 33 is removed therefrom through line 35. This product may be withdrawn from the system through line 36 or recycled through line 37 and pump 38 to the inlet side of heating coil 12 for further cracking treatment.

Vapours remaining uncondensed in the fractionating tower 32 and containing the desired distillate are removed overhead through line 39 which passes to a condenser 40 in which the desired liquid distillate is condensed. Products from the condenser 40 may be passed through a receiver 41 in which the liquid distillate condensed in the condenser 40 separates from the normally gaseous products formed in the cracking operation. The gaseous products may be vented from the receiver 41 through line 42 having a valve 43 for imposing the desired back pressure on the system. Liquid distillate forming the final product of the process is withdrawn from the receiver 41 through line 44 and may be subjected to any further finishing treatment desired for the production of a final, stable and marketable product. If desired, a portion of the distillate formed may be returned through line 45 and pump 46 to the top of frac-

tionating tower 32 as reflux medium therefor.

If desired a portion of the condensate may be passed through a cooler 49 and then injected into the stream of oil vapors passing to the fractionating tower to serve as a cooling medium to reduce the temperature of the vapors. If desired a cooling coil 50 may be provided in the bottom of the tower to provide the necessary amount of cooling to form the desired amount of condensate.

According to the invention, the heavy condensate withdrawn through line 34 is passed through line 51 and pump 52 to the inlet side of a heating coil 53 located in furnace 54. Conditions within the furnace 54 may be controlled to attain a substantial cracking of such oil into motor fuel during its passage therethrough, or it may be controlled so as to effect a mild viscosity breaking of said oil to form additional cracking stock for catalytic cracking.

The products from the coil 53 pass through line 55 to a chamber 56 which may serve as a liquid separator or as a coking vessel. The oil introduced into chamber 56 separates into vapors and unvaporized residue containing the catalyst. Liquid residue may be withdrawn continuously or intermittently from chamber 56 through line 57 or as previously described the residue may be maintained in the vessel 56 until converted to solid coke residue. In the latter case a plurality of coking vessels 56 may be arranged in parallel so that the coke can be removed from the individual vessels without interrupting the process.

Vapors liberated in the chamber 56 are removed overhead through line 58 and may be passed through line 59 to the fractionating tower 32 for fractionation. For simplicity a single fractionating tower is shown for fractionating products from the vapor phase catalytic cracking zone 22 and the cracking coil 53. In many cases, however, it is desirable to provide separate fractionating equipment so that products produced from each unit may be segregated.

In other cases the vapors may for example pass through lines 58 and 60 to the inlet side of the superheating coil 19 located in furnace 20 wherein they may be combined with the fresh feed being heated therein.

If desired, fresh oil from an extraneous source or a slurry of oil and catalyst may be introduced into line 51 through line 61 and treated along with the heavy condensate passing to coil 53. For example, residue from the separator 17 may be passed through lines 62 and combined

with heavy condensate passing to coil 53.

According to a modification, the products from the heating coil 53 without passing through the separator 56 may be passed directly through line 63 and merged with the fresh feed oil passing to the cracking converter 22 or the overhead from chamber 56 may be passed through lines 64, 64 and 63 to converter 22.

As a further alternative the heavy condensate containing the entrained catalyst rather than being subjected to separate heating or cracking treatment, before merging with the stream of fresh feed may be recycled directly to various points in the fresh feed circuit. For example, a part or all of the heavy condensate from line 51 rather than passing through the heating coil 53 may be passed through lines 65 and 66 to the separator 15 wherein it will combine with fresh feed from the heating coil 12. As another modification the heavy condensate may be passed through lines 65 and 67 and merged with fresh feed prior to being introduced into the heating coil 12, or as a further alternative such heavy condensate may be passed through lines 65, 68 and 69 to the inlet side of the superheating coil 19. In case all the heavy condensate from the fractionating tower is recycled to the same cracking circuit the coil 53 and separator 56 may be omitted or it may be employed for cracking an extraneous feed or crude residue from separator 15.

The catalyst contained in the heavy condensate stock formed in the bottom of the fractionating tower 32 is employed for further cracking treatment without attempt to separate such catalyst from the cycle oil. The amount of catalyst contained in the heavy condensate in the bottom of the fractionating tower 32 may be controlled by regulating the amount of powdered catalyst removed in the dry separators 27, 27' and 27¹. The amount of catalyst withdrawn from the system in dry form for regeneration may be controlled for example by providing by-passes (lines 69 and 70) around cyclone separators 27' and 27¹.

For simplicity the initial heavy condensate from the cracking operation has been described as formed in the bottom section of the main fractionating tower 50. It will be understood, however, that two separate towers may be provided for segregating the condensates or the initial condensate may be formed in an intermediate condenser in the line leading to the fractionating tower.

The temperature, pressure and other operating conditions employed in the process will depend upon a number of factors, such as the activity of the catalyst, char-

acter of the oil to be cracked, amount of conversion desired, and other factors. In general, it is preferred to operate the process at substantially atmospheric pressure except for the necessary inlet pressure required to obtain the desired flow through the system hereinbefore described. However, mild superatmospheric pressure such as of the order of from 5 to 20 atmospheres may be used. The fresh oil passing through the initial heating coil 12 may be heated to a temperature of from 700° F. to 850° F. and the oil passing through the vaporizing and heating coil 19 may be superheated to a temperature of from 800° F. to 1000° F. Due to the endothermic nature of the cracking reaction, the temperature within the reaction chamber 22 will be somewhat below the outlet temperature of coil 19. The temperature of the oil passing through the coil 53 may range from 800° F. to 900° F. and is preferably subjected to milder cracking conditions than are accomplished in the catalytic converter 22.

In our prior Specification No. 547,048 there is described and claimed a vapor phase catalytic conversion process of the kind in which a suspension of vapors and catalyst is passed through a heated reaction zone, wherein the catalyst is separated from the cracked vapors from the reaction zone by first passing such vapors through a cyclone separator in which the bulk of the catalyst is separated and then passing the vapors through a cooling zone to produce a condensate which is passed in countercurrent to the residual vapors in a second separation zone so as to scrub residual catalyst from such vapors.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. In the catalytic cracking of hydrocarbon oils to form lower boiling motor fuel products wherein the catalyst in finely divided state is suspended in a stream of oil to be cracked and the stream is passed in vapor form through a cracking zone maintained at cracking temperature, and in which the bulk of finely divided catalyst is separated from the cracked products while the latter are in vapor state, the vapors thereafter being partially cooled to condense a higher boiling fraction containing the remainder of said finely divided catalyst, the improvement comprising subjecting said higher boiling fraction to further cracking treatment.

2. A catalytic cracking process as claimed in Claim 1, wherein the higher boiling fractions containing the remainder

of said catalyst is combined with said original stream of oil and subjected to further cracking treatment therewith.

3. A catalytic cracking process as claimed in Claim 1, wherein said higher boiling fraction is subjected to further cracking treatment in a zone independent of the first named cracking zone.

4. A catalytic cracking process as claimed in Claim 1, wherein the catalyst is first mixed with the liquid oil and the resultant oil-catalyst slurry is passed through a vaporising zone.

5. A catalytic cracking process as claimed in Claim 1, wherein the oil is first vaporised and the catalyst is introduced in a dry state into the oil vapors.

6. A catalytic cracking process as claimed in any of Claims 1 to 3, wherein the high boiling fraction is passed through a heating zone maintained at a temperature sufficient to convert said high boiling fraction into vapors and a solid residue, the products from said heating

zone are passed into an enlarged heating zone wherein the unvaporised products are maintained for a period sufficient to produce therefrom a solid residue, and the vapors from said heating zones are fractionated to segregate a motor fuel fraction therefrom.

7. A process according to Claim 1, wherein the condensed higher boiling fractions containing the remainder of the catalyst are subjected to further treatment together with an unvaporised residue obtained by preheating hydrocarbon oil to be cracked to a temperature sufficient to vaporise a substantial portion but not all thereof.

8. The improved catalytic cracking process hereinbefore described with reference to the accompanying drawing.

Dated this 21st day of May, 1941.

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[This Drawing is a reproduction of the Original on a reduced scale.]

